Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

XVII.

NOTE ON THE VARIATION OF MOLECULAR PRESSURE.

By Carl Barus.

Presented December 9, 1891.

1. *The Method.* — If a quantity of heat, δQ, be imparted to a substance, the result is usually expressed as $\delta U + \delta U'$, where δU is the internal, and $\delta U'$ the external work done. For liquids at atmospheric pressure, $\delta U'$ is negligible.

Regarding δU from an experimental point of view, two salient considerations present themselves. If I measure latent heats (λ), δU includes both the dissociation energy and the expansion energy necessary to effect fusion, as follows: —

a. The dissociation energy per gram necessary to change the solid molecule into the liquid molecule, isothermally, without change of volume.

b. The energy per gram for the isothermal expansion of the molecule.

c. The energy per gram for the isothermal expansion of the configuration of molecules which constitutes the given substance from solid to liquid.

If I measure specific heats isopiestically, δU includes the purely thermal energy necessary to effect changes of the body's temperature and the expansion energy, viz.: —

d. The purely kinetic energy per gram per degree, by which the solid is appreciably changed as to temperature. This is a temperature function only.

e. The energy per gram for the corresponding isothermal expansion of the molecule.

f. The energy per gram for the corresponding isothermal expansion of the configuration of molecules; with similar quantities, d', e', f', for the solid state.

The permissibility of thus separating δU into a thermal (temperature) and a volume and thermal component is given, if the isometrics are straight lines.* For liquid thymol this is very nearly true. § 10.

2. In relation to *a*, I shall postulate: (1) A liquid or a gas solidifies whenever, in consequence of changes of the physical or chemical environment (temperature, stress external or internal, etc.), the cohesive valency of the constituent atoms is sufficiently increased to admit of the permanent construction of a tridimensional chain, the type structure and the molecular weight of which (solid) are each a multiple of the given structure and molecular weight. (2) A gas liquefies whenever in consequence of changes of environment the cohesive valency of the constituent atoms is increased, without affording means for the permanent construction of the chain in question.

Thus, it is supposed that the same molecular nucleus is present in the three states of aggregation, and that the aggregations are produced by relatively weak affinities. Since, therefore, it is my purpose *to bring these forces to bear*, at constant external pressure, *when the molecules are at successively different distances apart*, it will facilitate reasoning to assume at the outset that the energy necessary to effect the change *a*, § 1, is constant as to temperature, at least within the interval 0° to 50°, under experiment. §§ 8, 9, 12.

3. In relation to *b* and *c*, § 1, conjointly, I will proceed as follows. Anywhere within the given body let a small sphere be described; and conceive the expansion work between solid and liquid done within this sphere by the applied heat to be represented by the isothermal expansion against a pressure, p, acting on the surface of the sphere. Then p may be called the molecular pressure and the expansion work will be,

$$w = \int p\, dv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

4. Now, if a substance can be found which under the same pressure may be kept either in the solid or in the liquid state through a considerable range of temperature, then if the latent heats within this range regarded as functions of temperature, be co-ordinated with the corresponding volume changes solid-liquid, relations for the energies *b* and *c*, § 1, are deducible.

Again, if with the knowledge of *b* and *c* in hand, specific heat regarded as functions of temperature, be co-ordinated with the corresponding thermal expansions, the characters of the energies *e* and *f*, for the solid and the liquid state, respectively, are more nearly ripe for discussion.

---

* Fitzgerald, Proc. Roy. Soc., Vol. XLII. p. 50, 1887.

This, in brief, is my method. What it thus far has yielded I will now indicate.

5. *Thermal Expansion.* — In virtue of the occurrence of volume lag,* or hysteresis, substances of the kind needed in § 4 are forthcoming. I infer, therefore, that as regards isopiestic thermal expansion the liquid and the solid, as well as the gas, obey certain ideal laws, which may be conceived to hold good even though temperature be decreased below condensation or solidifying points, indefinitely.

I have worked with the beautifully crystalline solid thymol, which melts slightly below 50° C., and when freshly distilled can be cooled even below 0° C.

TABLE I. — EXPANSION OF THYMOL, $v = \frac{v_0}{1 - k\theta}$.

Substance.	$v_0 \times 10^5$.	$k \times 10^7$.	Temperature Interval.	No. of Observations.	Remarks.
Solid	96293	$2300 + 9\theta$	0° – 32°	8	Pyknometer measurements.
"	96369	2456	0 – 34	10	Expansions of powdered thymol under water.†
"	*96306*	*2456 + 2* θ	0 – 33	10	
"	96579	$2300 + 3\theta$	0 – 34	6	Expansions of a single lump under mercury ‡
"	96565	$2200 + 6\theta$	0 – 34	5	
"	96565	$2260 + 6\theta$	0 – 41	7	
"	96584	$2100 + 9\theta$	0 – 44	10	
Liquid	*101128*	*7600 + 2* θ	0 – 46	12	Pyknometer measurements.
"	101128	$7500 + 6\theta$	0 – 53	5	Pyknometer measurements, liquid boiled in vacuo. Air also expelled by vacuum solidification.

---

* Am. Journal, Vol. XLII. p. 125 *et seq.*, 1891. Cf. Vol. XXXVIII. p. 408, 1889; Vol. XXXIX. pp. 490–494, 1890.

† Evaporation in the first set not allowed for; hence the high $v_0 = .96369$.

‡ The lump unavoidably contains vacuities and fissures within. Powdered thymol cannot be put under mercury, free from air.

Measurements of thermal expansion made with a variety of methods gave me the data of Table I. They have been conveniently put in the form of an equation (Mendeleeff), $v = v_0 / \overline{1 - k\theta}$, where v is the specific volume of thymol at θ° C., and k is all but constant as to temperature.

The discrepancies here observed are easily explained, being in part due to unavoidable insufficiencies of the methods, and in part to the special properties of thymol. The numbers in Italics correspond to the conditions under which the calorimetry must be done, and are therefore selected.

It will be seen that at zero the difference of specific volumes solid-liquid is about .0485 c.c., whereas at 50° the same difference has increased to .0760 c.c., an increase of more than 50%. This cannot be regarded as a mere differential. Indeed, the relations are such that the curves if prolonged intersect at about —100°, after which the volume of the solid exceeds that of the liquid. In other work * I referred to the same point as the transitional temperature, and inferred it from the tendency of the volume lag to vanish when temperature is decreased below a certain value. The new evidence in favor of a continuous passage of the normal type of fusion into the ice type is noteworthy. Solidification contraction decreases with temperature at a rate very much more rapid than the coefficients of expansion.

6. *Latent Heat.* — A general survey of my best results for latent heat (λ) are given in the following table, for the intervals of temperature specified.

TABLE II. — LATENT HEAT OF THYMOL VARYING WITH TEMPERATURE.

Temperature Interval.	λ	Temperature Interval.	λ	Temperature Interval.	λ
° °		° °		° °	
3.2–5.1	23.0	25.9-30.7	26.3	35.6-37.7	22.6
4.2–6.1	23.4	25.8–30.4	26.9	35.1–39.0	23.4
2.5–4.7	24.8	25.8–30.4	26.9	36.2–39.2	22.7
		25.7–30.3	26.9	36.0–39.6	26.0
				36.4–39.9	23.7
Mean. 4°.9	Mean. 23.7	Mean. 28°.1	Mean. 26.8	Mean. 37°.5	Mean. 23.7

---

* Am. Journal, Vol. XLII. p. 145, 1891.

The difficulty in obtaining such results is excessive; for, apart from the serious complications of the method itself, (thus it takes hours before complete solidification sets in at the higher temperatures, and minute stages must be observed in order to allow for radiation,) the observer is dealing with an (under-cooled) substance, which at the mere suggestion of careless handling begins to freeze prematurely, and which in the liquid state tends to become impure by absorption of air or water vapor. These decompositions are gradual, yet they cannot be disregarded, because they lower the melting point and thus induce early partial fusions and late complete solidifications. The table also shows the difficulty in working at other than room temperature.

7. *Specific Heat.* — For the reasons just stated, I shall have to give my data for the specific heat of thymol provisionally; for though I made such experiments with great care and in considerable number, I was not at the time fully conversant with the variety of precautions to be taken to keep the substance pure.

TABLE III. — Specific Heat of Solid and of Liquid Thymol.

Substance.	Temperature Interval.	Specific Heat.	Substance.	Temperature Interval.	Specific Heat.
Solid	20°-32°	.388	Liquid	25°-54°	.508
"	22-43	.430			
Solid	22-32	.374	Liquid	22-38	.506
"	22-43	.429	"	23-51	.515
"	22-48	.643			
"	24-49	.969			
Solid after distillation	26-41	.504	Liquid distilled	26-42	.509

These data, obtained with different charges, are much below the sensitiveness of the method. The values for solid thymol, moreover, show the unreasonably large influence of temperature, accounted for in § 6.

8. *Molecular Pressure.* — Taking the data of Table II. at their face value, the only justifiable conclusion to be derived is that λ is constant for the interval 0° to 40°. Within the same interval the differ-

ences of specific volume increase from .048 c.c. to .071 c.c., nearly 50%. Hence, if either of these quantities be more than a vanishing increment, their difference must also be.

From a different point of view: if the dissociation energy, q, is large as compared with the expansion energy, then the thermal constancy of λ is of little consequence here. I make the supposition, therefore, that q is not large relative to $\int p\,dv$, a point which I will endeavor to test in § 12.

Returning to equation (1), § 3, it therefore follows experimentally that

$$q_0 + \int_{v_0}^{V_0} p\,dv = q + \int_{v}^{V} p\,dv \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where q_0 and q are the dissociation energies, p the molecular pressure, v_0 and V_0 the specific volumes solid and liquid respectively at zero Centigrade, and where v and V have the same meaning at any given temperature between zero and the melting point. If by § 2, $q_0 = q$, then equation (2) may be reduced to

$$\int_{V_0}^{V} p\,dv - \int_{v_0}^{v} p\,dv = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

an equation in which the molecular pressure is expressed in terms of the thermal expansion of the liquid and the solid within the same thermal limits, and by which any reasonable law of internal pressure may be preliminarily tested.

Now suppose these integrations be successively taken at zero, and all succeeding stages up to the melting point: then will the distance apart of the limits of either term vary in any ratio relative to the distance apart of the limits of the other. An equation

$$p\,(V - \varkappa) = c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

will therefore at least partially satisfy (3). In how far it may do so throughout the whole interval 0° to 50° may be gauged by determining the constancy of $\varkappa$ throughout this interval. This is done in the next table, where v, V, and $\varkappa$ are given for successive temperatures θ.

The constancy of $\varkappa$ is thus marked, and quite within the range of experimental errors; and hence the equation (4) expresses the law of force as well as any other function fitted to equation (3).

TABLE IV. — VALUES OF κ.

θ	v	V	κ	Mean κ
0°	.96300	1.01128	.94140	.94145
30	.97035	1.03508		
10	.96540	1.01905	.94148	
40	.97289	1.04334		
20	.96785	1.02698	.94148	
50	.97550	1.05178		

Since $\varkappa$ is the minimum volume to which the liquid may be reduced when pressure increases indefinitely, it is interesting to note that this volume is $(1.05 - .94)/1.05$, or 10% below the liquid volume at the melting point. Amagat* found that even at 3,000 atm. the volume of water at 17°.6 was not decreased more than 10%. Again, $\varkappa = .9415$ is very near the volume of solid and liquid thymol at the transitional temperature, this volume being .9420. Thus throughout this tentative work a certain degree of consistency is apparent, always remembering that the approximations $q_0 = q$ and $p_0 = p$ is not vouched for.

9. Equation (4) may be regarded as a point of departure from which the further construction of the equation may be attempted. Thus it is next in place to endeavor to ascertain how temperature may be said to lurk in the quasi constant, $p\ (V - \varkappa)$. In a substance like thymol, which boils at 233°, the interval 4°–40° is too small to bring out thermal variations appreciable by the above method. Hence the deduction from (2), if $p\ (V - \varkappa) = \varphi\ (T)$, though easily integrable, is not as yet available. I have therefore sought to throw some light on the thermal variations of p, and on the relative importance of $q - q_0$ by other methods.

In the first place I will note the possibility of getting rid of considerations relative to the thermal variation of the dissociation energy, q, as follows.

Suppose the specific heat at constant volume is the same for the liquid and for the solid, kept at the same volume and temperature. Suppose also that the solid and the liquid isopiestics for a given pressure do actually intersect at the transitional temperature, § 5. If, therefore, the latter be taken as a point of departure, the total energy communicated to the liquid up to the temperature t and volume V, when a is the transitional volume, will be

---

* Amagat, Compt. Rend., Tom. CIII. p. 429, 1886. According to Rücker (Nature, Vol. XLI. p. 362, 1890) converging lines of evidence show that liquids cannot be compressed more than .2 or .3 of their normal bulk.

$$q + \int_a^V P\,dV + F(t),$$

where the three terms represent dissociation, expansion, and purely thermal energy, respectively. The corresponding total energy imparted to the solid up to the temperature t will be

$$0 + \int_a^v p\,dv + f(t),$$

a being the common volume at the transitional temperature. The difference between these quantities is the latent heat, λ, at t. Hence the increase of latent heat from t_0 to t will be, (since λ is constant, and $F(t) - f(t)$ is assumed to be constant,)

$$\int_{V_0}^V P\,dv + \int_{v_0}^v p\,dv = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3')$$

an equation which differs from equation (3) in so far as P and p denote the internal pressures for the liquid and the solid states respectively, under conditions in which external pressure is pronouncedly variable. The equation (3′) would still apply if the specific heats at constant volume differ only by a constant appreciably within the limits of observation (0°–50°), but it is not available for practical comparisons.

10. *The Isometrics.*—Some time ago I showed* that within a range of 1,000 atmospheres of external pressure, at least, and within reasonable limits for the thermal stability of organic bodies, the isometrics of liquids, and particularly of thymol,† are very nearly straight. Thus the extension of equation (4) would be

$$(p + p')\;(V - \varkappa) = c\,T,$$

---

* Phil. Mag., (5,) Vol. XXX. p. 348, 1890.

† Ibid., p. 358, and Plate XI.

where p' is the external pressure and T is temperature. In my experiments, only a single value of volume is introduced, and hence the work is not further available. Referring to the intrinsic equation of Ramsay, Young, and Fitzgerald (*loc. cit.*, p. 51),

$$p' = R\,T\,/(v - v_0) - \mu/v^n,$$

so that here the internal pressure has the form $p = \mu/v^n$.

11. *Isothermals.* — The question ceases to retain so simple an aspect when the isothermals of liquids are considered. Of the two equations which I discussed in my work* on the compressibility of liquids, viz.:

$$\frac{dV}{dp'} = -\frac{\theta}{1 + \alpha p'} \quad \text{and} \quad \frac{dV}{dp'} = -\frac{\mu}{(1 + \nu p')^2} \quad . \quad . \quad (6)$$

where p' is the external pressure, and θ, α, μ, ν are constants, the latter is at once compatible with the results of § 9. For equation (3) leads to

$$\frac{dV}{dp} = -\frac{\phi\,(T)}{p^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and hence in equation (4), $1/v = p$ is the internal pressure active under the isothermal circumstances of compression, and

$$\phi\;(T) = \mu\,/\,\nu^2.$$

The results actually found for thymol are given in Table V., T being the absolute temperature of the isothermals, and pressures being in atmospheres.

TABLE V. — COMPRESSIBILITY OF THYMOL, $\dfrac{dV}{dp} = -\dfrac{\mu/\nu^2}{(1/\nu + p')^2}$.

T	$\mu \times 10^6$	$\nu \times 10^6$	$1/\nu$	μ/ν^2	Remarks.
°			Atm.		
301	66	300	3370	750	Initial pressure, $p'_0 = 20$ atm.
338	73	330	3050	680	Interval of observation, 400 atm.
373	97	435	2300	510	$\mu/\nu = \text{const.} = .222$.
458	162	730	1370	304	Melting point, 49°.5 C.
583	481	2160	460	102	Boiling point, 233° C.

---

* Am. Journal, (3,) Vol. XXXIX. pp. 497 and 506, 1890.

Thus it is seen that the internal pressures ($1/\nu$) decrease from a value of nearly 4,000 atm. at zero Centigrade, indefinitely. The same is true of μ/ν^2, but in neither case are the observations sharp enough to indicate the nature of this variation. Indeed, to co-ordinate all the results, I used the smoothing process $\mu/\nu =$ const. Hence I shall have to sketch the mere trend of the data here involved, by grouping the values μ/ν^2 along some mean straight line like $.29\ (560 - T) = \varphi\ (T)$, wherein preference is given to low temperatures. Thus the volume equation takes the form

$$(V - \varkappa) = \frac{2.9\ (560 - T)}{p + p'} \quad . \ . \ . \ . \ . \quad (8)$$

When $p = -p'$, the liquid will boil, and consequently, since $v - \varkappa$ remains finite, $T = 560$. This number stands not unreasonably for the absolute boiling point of thymol at the external pressure p', which in the last table is 20 atmospheres.

12. The question now arises how the result (8) compares with the calorimetric equation

$$q + \int_v^V p\, dv = \lambda,$$

where $\lambda = 25$ is at the outset considered constant as to temperature.

Availing myself of equation (8), expressing pressures in degrees per square centimeter instead of in atmospheres, and remembering that Joule's equivalent is 4.2×10^7, I find

$$\int_v^V p\, dv = \frac{2.9}{42} \times (560 - T) \times ln\, \frac{V - \varkappa}{v - \varkappa} \quad . \ . \ . \quad (9)$$

Table IV. shows that throughout the interval 0° to 50°

$$ln\, (V - \varkappa)\ /\ (v - \varkappa) = 1.18 \text{ nearly.}$$

Hence the values of the dissociation energy q are in gram calories,

0°	$p\, dv = 23.4$	$q = 1.6$
20°	21.8	3.2
40°	20.1	4.9

Thus the dissociation energy is small as compared with the expansion energy; but q increases with temperature which is unreasonable. To explain this discrepancy it is necessary to revert to Table II., supposing the constancy of λ no longer tenable. Thus it appears that the march of q is within the errors of λ, and hence it has no meaning. Cf. § 9. It follows, in general, therefore, that the results obtained in measurements of the compressibility of thymol are not inconsistent with the calorimetric data; and it has thus been brought out, inasmuch as the dissociation energy is not large relative to the expansion energy, that the premises of § 8 are sustained.

13. *Energy and Volume.* — I have finally to touch upon the data obtained for specific heat, and their bearing on the purely thermal energy of thymol. It is interesting in the first place to compare the heat absorbed per unit of volume increase in the solid state, the liquid state, and during the change of state from solid to liquid. This has been done in the following table.

TABLE VI. — VOLUME RELATIONS OF THERMAL CAPACITY.

Liquid Interval 22° to 38°.	Fusion.	Solid Interval 22° to 32°.
Mean spec. heat, .506	Latent heat, 25.4	Mean spec. heat, .381
Mean volume increase .01307 c.c.	Volume increase, .0589 at 19°.3 .0655 at 31°.8	Mean volume increase . . .00250
Coefficient .000817		Coefficient . .00025
Ratio $\frac{\Delta Q}{\Delta v}$ 620	430 390	1520

Thus it appears that the energy expended per unit of volume increment is in marked degree greater for the solid than for the liquid state, and is greater in both of these states than during the intermediate fusion.

14. Sufficient data are now in hand for the computation of the specific heat at constant volume of thymol. Applying the well known thermodynamic relations (cf. Clausius, Chap. VIII., § 5) at 29°, Table V. shows $(d\,V_\theta/dp) = 66/10^{12}$ in terms of dynes per square centimeter and atmospheric pressure nearly. Under the same conditions $(d\,V_p/d\,\theta) = 801/10^6$ from Table I. Hence the specific heat at constant volume C_v is, from Table III.,

$$C_v = .506 - \left((29 + 273)/42 \times 10^6\right)\left((801)^2/66\right) = .436,$$

or about .86 of the specific heat at constant pressure $C_p = 506$.

The value $C_v = .44$ is larger than the solid specific heats at constant pressure for the same interval (Table III.), and hence *a fortiori* larger than the corresponding solid specific heats at constant volume, which are as yet indeterminable. § 9.

With this result, a direct computation based on equation (9) above may be compared. Integrating between 22° and 38° (Table VI.), — i. e. between the specific volumes 1.02860 and 1.04167, — the expansion energy is found to be 2.56 to 2.42 g. cal., according as the molecular force at the beginning or the end of the interval is inserted. The total energy imparted within this interval is $.506 \times 16$. Hence the purely thermal energy per degree between 22° and 38° has the mean value of .35, or about two thirds the specific heat at constant pressure.

Compared with the preceding datum, .44, this result is considerably too small; i. e. the expansion energy applied is about twice as large as its true value. I might point this out as an indication of the difficulty encountered in deducing internal pressure from the curvature of the isothermals (§ 11) ; but the true nature of the discrepancy is an error in principle, since the change of internal pressure with temperature must be radically different when the body is kept at constant external pressure in one case, and at constant volume in the other. Hence I do not regard the present result as conflicting with § 12.

15. *Melting Point and Pressure.* — The data of Tables I. and II. suffice for a preliminary computation of this value. Using the notation of Clausius (Wärmetheorie, Chap. VII., § 2), Table I. shows that at $T = 50°$ (melting point, nearly), $\sigma - \tau = .0763$. From Table II. the mean value (0°–50°) of r' is 24.7, the minimum value 23, and the maximum 27. Hence, if pressures be expressed in atmospheres instead of dynes per sq. cm., the mean relation of melting point to pressure is $d\,T/dp = .024$; or, more clearly,

$$.025 > d\,T/dp > .022,$$

where the upper limit is probably more nearly correct. This value lies well within the margin of data (.020 to .036) thus far in hand, and found with wax, paraffine, spermaceti, and naphthalene. From a perusal of my work on the continuity of solid and liquid,* it appears clearly, however, that a more accurate value of $d\,T/dp$ is obtainable from direct experiment, from which a value for latent heat may then be computed by inverting the thermodynamic equation.

---

* Am. Journal, Vol. XLII. p. 144, 1891.

16. In the above paragraphs I have endeavored to exhibit the stage of progress attained in the work on molecular pressure, at the time when it had to be abandoned; for the calorimetric work can only be satisfactorily done in midwinter. Cf. §§ 5, 6, 7. It will be seen, I think, that the subject, as a whole, is ripe for sharper tests, and the work will therefore be resumed at an early opportunity.

Physical Laboratory, U. S. G. S.,
Washington, D. C.